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Energy Fuels, **Just Accepted Manuscript** • DOI: 10.1021/acs.energyfuels.6b01556 • Publication Date (Web): 01 Sep 2016

A Study on Reduced Chemical Mechanisms of Ammonia/methane Combustion under Gas Turbine Conditions

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ABSTRACT: As an alternative fuel and hydrogen carrier, ammonia is believed to have good potential for future power generation. To explore the feasibility of co-firing ammonia with methane, studies involving robust numerical analyses with detailed chemistry are required to progress towards industrial implementation. Therefore, the objective of this study is to determine a reduced mechanism for simulation studies of ammonia/methane combustion in practical gas turbine combustor conditions. Firstly, five different sized reduced mechanisms of the well-known Konnov's mechanism were compared. The reduced mechanisms were tested for ignition delay time validation (0D) using ammonia/methane mixtures at high pressure conditions relevant to gas turbine devices. Furthermore, the combustion products of ammonia/methane premixed laminar flames (1D) were validated with the results from the full Konnov's mechanism. Finally, CFD simulations of a turbulent flame (2D) with all the reduced mechanisms were performed under high temperature and high pressure conditions representative of industrial systems. Results show that several of the reduced mechanisms utilized performed reasonably well in combustion simulation studies under gas turbine conditions. Hence a reaction mechanism with 48 species and 500 elementary reactions is recommended for future studies.

1 INTRODUCTION

In the context of ever increasing energy demand and pressure to reduce CO_2 emissions from power generation, alternative fuels have been widely studied with great concern. Among the proposed renewable fuels, ammonia has been drawing much attention as a clean fuel recently. Since ammonia has a high hydrogen density, it can be seen as a hydrogen vector, but without the storing and transportation barriers associated with hydrogen utilization. Thus, ammonia has the potential to become a promising green fuel just like hydrogen[1-5], burning in an environmentally acceptable way, yielding no carbon dioxide. Ammonia also has advantages in its production, delivery, storage, handling and distribution through existing infrastructures and experience.

Currently, there are several examples and studies trying to utilize ammonia for power systems, particularly utilizing internal combustion engines [4-6]. However, power obtained from such units is relatively modest, typically in the 0.1 – 1.0 MW range. Thus similarly responsive but larger power generators will be required to meet the demands of electrical grids. As a result, considering the pressure to reduce carbon dioxide emission and finite resources of fossil fuels, using ammonia in gas turbines for power generation is an interesting proposition. "Green" ammonia can be produced from any renewable source. However, there is still a dearth of information relating to the utilization of ammonia in gas turbine combustors.

Although research has been undertaken for operational flame limits, chemical models, flame speed and trials in internal combustion engines, gas turbine utilization has not been studied extensively [7-9]. Previous results show a series of challenges when utilizing this fuel, including: a) lower flame temperatures and slower kinetics; b) stability and efficiency problem; c) requirements for pre-vapourising the ammonia ; d) pre-cracking of the molecule to improve ignition reliability and increase burning rate. NASA also identified during their XLR-99 programme the need for "combustor enhancers" such as hydrogen, gasoline, kerosene, propane, etc., especially during start-up and idle [10]. Another potential fuel enhancer is methane, as this is the main fuel of gas turbines for power generation. An ammonia/methane blend could be used not only from green ammonia sources, but also from by-product ammonia obtained from industrial processes. Ammonia addition could support peak-hour energy consumption requirements with fuel cost reduction. For instance, an immediate beneficiary of this blend could be steelworks companies that produce ammonia as a by-product of coke oven gas cleaning[11, 12]. More recently, a new research program "Power to Ammonia" has initiated in the Netherlands looking into

potentially turning gas-fired power plants into 'super batteries' [13]. Initial tests will focus on co-firing ammonia with methane in order to determine fuel blends that cause the lowest impact on gas turbine systems in order to reduce retrofitting costs in currently running facilities. Therefore, this research appraises ammonia/methane as the fuel to be studied for the purpose of application in gas turbine combustion for large scale power generation in these energy intensive industries [14-18].

Developing a computational fluid dynamics (CFD) based methodology alongside complex chemistry can help to capture more accurate information for the prediction of NOx emissions, turbulent reacting flows, combustion dynamics, autoignition, etc. Therefore, to utilize ammonia/methane effectively in a gas turbine, CFD simulations can serve as a powerful tool for analysing and designing ammonia combustion systems. However, the large numbers of species and reactions in detailed mechanisms make it almost impossible to conduct CFD simulations with detailed chemistry for practical complex combustion systems such as a gas turbine combustor. For instance, the mechanism used in this study, the Konnov's mechanism [19], has over 100 species and 1,200 reactions. Using a reduced reaction mechanism instead of a detailed one can substantially decrease the computational time and memory requirement, thus making feasible large scale calculations for practical gas turbine combustors with complex chemistry. However, there are very few studies [20, 21] concerning the use of reduced mechanisms for ammonia combustion under gas turbine conditions. Morevoer, these reduced mechanisms are developed based on a single fuel composition not including the presence of CH_4. Furthermore, no research concerning ammonia combustion mechanism reduction has been tested with multi-dimensional CFD simulation. Thus, there is a need to reduce detailed ammonia/methane combustion mechanisms in order to apply them to CFD simulation for practical gas turbine combustor research.

Due to the breadth of previous validation studies for Konnov's mechanism, it was an obvious choice for the simulation of ammonia/methatne combustion in this study. Kumar et al.[17] showed that Konnov's mechanism is the most adept at predicting ammonia based combustion for fuel mixtures in a jet flame for the four mechanisms considered. Duynslaegher, Contino et al. [20] improved Konnov's kinetic mechanism and then reduced it for use in a SI engine numerical simulation. Nozari [21] conducted a numerical study of laminar flame speed and NO_x emission for NH_3/H_2 mixtures at elevated pressure conditions using a validated Konnov mechanism. Duynslaegher et al. [22] studied the laminar burning velocity, flame temperature and species concentrations using Konnov's mechanism at elevated pressures and temperatures. Duynslaegher, Jeanmart et al.[23] simulated an ammonia/oxygen/hydrogen/argon premixed flat flame using Konnov's mechanism. Across the four mechanisms used in that study, Konnov's mechanism demonstrated the best performance for prediction of species mole fraction profiles across the flame. Hence, to date, Konnov's kinetic scheme has shown the best performance for the combustion of ammonia-based fuel amongst the range of mechanisms tested in previous studies.

Hence, in this study reduced variations of the Konnov mechanism are compared to existing experimental data to appraise the suitability of representing ammonia/methane combustion kinetics under conditions of typical gas turbine combustion. The aim is to find a reduced mechanism to represent the kinetics of ammonia/methane combustion with sufficient accuracy under elevated pressure and temperature conditions. Considering the strong turbulence and interactions between turbulence and chemistry in gas turbines, the differences between the reduced mechanisms can potentially lead to significant deviation in final results for CFD simulations. Therefore in this study not only ignition-delay times and laminar flames of NH3/CH4 are validated with the reduced mechanisms, but also turbulent combustion has been investigated to validate the performance of the proposed reduced mechanisms in more practical environments. Thus a comprehensive comparison in different dimensional levels (0D, 1D, 2D) is performed to generate and assess reduced kinetic mechanisms of ammonia/methane combustion under gas turbine conditions.

2 Reduced Konnov Mechanisms

Table 1. Full Konnov and Reduced Mechanisms

Name	No. Species	No. Elementary Reactions
Konnov [19]	129	1231
Mech.1	84	940
Mech.2	77	874
Mech.3	61	687
Mech.4	48	500
Mech.5	31	243

The full Konnov model comprises 129 species participating in 1231 reactions. This model has been reduced with the path flux analysis methodology described by Sun et al. [24] and Gou et al. [25] and implemented in their Chem-RC software[26]. The path flux analysis methodology ranks the importance of the chemical reactions and their

participating species based on the magnitude of the reacting flux through each species as determined for a series of baseline simulations of the detailed model. For this study, the detailed model was evaluated with homogeneous (ignition delay) simulations and with extinction curves generated by perfectly stirred reactor (PSR) simulations. For each case, mixture mole fractions of $NH_3/CH_4/O_2/N_2$ 0.088/0.0565/0.1795/0.675 corresponding to stoichiometric fuel-in-air conditions for a NH_3/CH_4 molar ratio of 61/39, which is the same ratio as that utilized in a generic swirl burner experimental campaign in [14]. For the constant volume ignition delay type calculations temperatures of 1000 K, 1200 K, 1500 K and 1800 K are used with pressures of 1 atm, 5 atm 12.5 atm. For the perfectly stirred reactor calculations an initial temperature of 300 K and maximum residence time of 33 seconds are selected, with simulations executed again at 1 atm, 5 atm 12.5 atm.

In assessing the importance of each reaction, the analysis considers the magnitude of the flux through both the "first generation" species participating in each (initial) reaction and the "second generation" species which result from the participation of the product species of the initial reaction in the other reactions described by the model. The importance of each species is then quantified by an interaction coefficient index. A series of reduced models are produced (of 31, 48, 61, 77 and 84 species) by exercising a threshold index (of 0.6, 0.3, 0.215, 0.15, and 0.05 respectively) where only species with an interaction coefficient index greater than the selected threshold index are included in each particular reduced model.

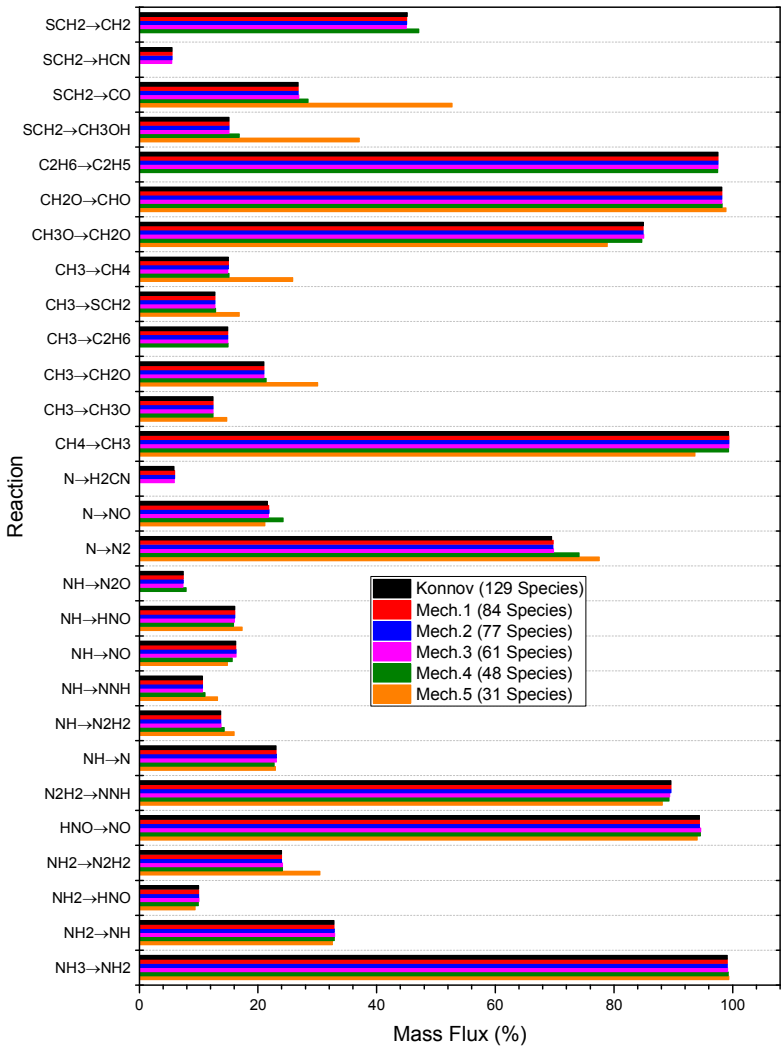


Figure 1. Species mass flux simulated with the Konnov and each of the reduced models in a constant volume perfectly stirred reactor for a fuel mixture of NH_3/CH_4: 61/39 at E.R.=1, 17 atm and 1550 K.

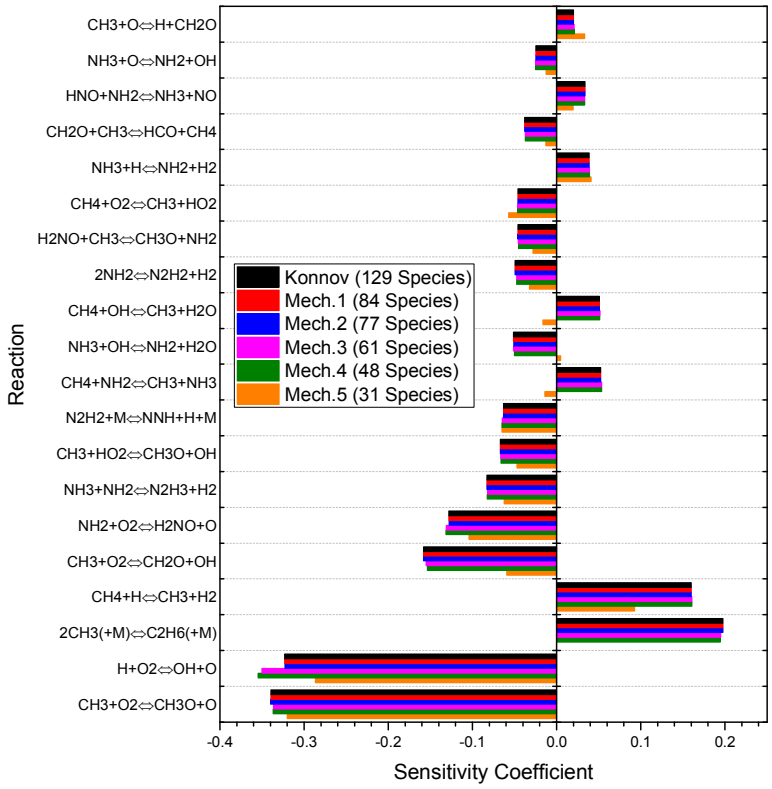


Figure 2. Sensitivity analysis of major reactions to ignition delay time for Konnov and each of the reduced models in a constant volume perfectly stirred reactor for a fuel mixture of NH_3/CH_4: 61/39 at E.R.=1, 17 atm and 1550 K.

To compare the validity of each of the reduced models, chemical flux and sensitivity analyses of a stoichiometric fuel in air mixture of NH_3/CH_4 (61/39) was performed under constant volume, homogenous and constant internal energy conditions of 1550 K and 17 atm. The results are presented in Figure 1 and 2 respectively. The flux analysis clearly shows how well the reduced models Mech.1-4 capture the flux behaviour of the original Konnov model. It is only when the species number is reduced to <40, as is the case with Mech.5 that a significant digression from the behaviour of the Konnov model is noted. For example, as ethane (C2H6) was excluded as a species from Mech.5, CH3 may not be consumed by recombination to C_2H_6, as is the case in the others models, therefore the model over predicts the mass flux to other avenues such as $CH_3 \rightarrow CH_4$, $CH_3 \rightarrow SCH_2$, $CH_3 \rightarrow CH_2O$ and $CH_3 \rightarrow CH_3O$. This pathway allows the rate of radical propagation/branching to be increased relative to the detailed model where methyl recombination to ethane is an important reactivity slowing the radical chain termination step.

Figure 2 shows a comparison of sensitivity analysis of the reactions effecting the ignition delay time for each reduced model. A negative value indicates that a reaction reduces the ignition delay time. For most models the $CH_3 + O_2 \Leftrightarrow CH_3O + O$ reaction was the most sensitive. However, for Mech.3 and Mech.4 the most sensitive reaction was the $H + O_2 \Leftrightarrow O + OH$. This shows an important degrading in the fidelity of the oxidation description, as the major radical chain branching reaction switches between a methyl radical dominated system, to one dominated by the hydrogen atom in Mech. 3 and 4. As expected, Mech.5 shows the largest deviation from the Konnov model and even opposing behaviour for the reactions of $CH_4 + OH \Leftrightarrow CH3 + H_2O$ and $CH_4 + NH_2 \Leftrightarrow CH_3 + NH_3$. The third most sensitive reaction for all models was the $2CH_3(+M) \Leftrightarrow C_2H_6(+M)$, however for Mech.5 the species C_2H_6 was excluded thus this reaction does not take place in the model. These omissions likely invalidate this reduced model as an accurate representation of ammonia/methane oxidation mechanism. Mech. 1 and 2, show very close important similarity to the detailed model, and are therefore recommended for use. In addition, the more severely reduced Mech. 3 and 4 also bare close resemblance to the detailed description, but do show of modes degradation in fidelity. This analysis highlights the limitations of such reduced models in their ability to capture the reactivity of the original Konnov model.

Although the less species and reactions there are in the reduced mechanism, the more computational cost can be saved, it is still needed to retain a balance between the accuracy and efficiency for the use of the reduced mechanisms in simulation studies. Therefore, based on the calculated results, five reduced mechanisms were obtained as choices for their

application in computational simulations. In the following study, the reduced mechanisms are shown as in Table 1. The five reduced mechanisms are available in 'Supporting Information'.

3 METHODOLOGY

3.1 Ignition Delay Time Simulation. Numerical prediction of ignition delay times is helpful in understanding autoignition parameters, detailed kinetics and reduction of detailed mechanisms. In fact, as an important well-known validation technology, computational prediction of ignition delay times is usually compared with shock-tube experiments [27-29]. In this study, ignition delay times were modelled with a closed homogeneous reactor in CHEMKIN-PRO [30]. In this model, the ignition delay time can be defined based on different criteria such as the time at which a certain species reaches the maximum concentration or the time at which an inflection point appears in pressure or temperature profiles [27, 29, 31]. In the simulation, ammonia and oxidiser mixtures are highly diluted (98-99%) to minimize viscous effects, heat transfer and non-equilibrium as performed in shock-tube experimental conditions [32]. As adopted by several previous researchers[33-35], a standard approach for such ignition calculations is to use constant-volume, adiabatic boundary conditions. The numerical work was carried out under a wide range of pressures, temperatures and equivalence ratios to simulate the experimental results of ammonia combustion provided by Mathieu et al [31], [36]. The reduced mechanisms obtained above were tested to validate their accuracy in predicting ignition delay times.

3.2. Burner Stabilized Premixed Flame Modelling. Burner-stabilized premixed flames were assumed to be one-dimensional and can be steady enough for accurate detailed experimental measurements of species profiles, temperature, flame speed, etc. As used in [37], simulation of this kind of flame can effectively model the chemical kinetics of ammonia/methane combustion process and help to interpret flame experiments. In this study, the burner-stabilized laminar premixed model in the Cantera software [38] was used to predict combustion products and emissions by different reduced mechanisms. The simulation was carried out under low pressure with different ammonia/methane ratios to simulate the experimental results of ammonia/methane combustion provided by Tian et al [37].

3.3. CFD Turbulent Combustion Modelling. To verify the performance of the reduced mechanisms further for the use of CFD simulation, a 2D model for turbulent flame combustion was built. The geometry of the burner consists of an inlet tube and a combustion chamber, Figure 3. The flame is stabilized down the dump in a recirculation zone by its sudden expansion. The burner is meshed with a structured grid of 13,575 cells. The modelling work is performed with Large Eddy Simulation (LES) coupled with complex chemistry. The CFD solver used for LES is from OpenFOAM toolbox [39], [40]. The case studied has a fuel mixture of 39%CH_4 and 61%NH_3 premixed with air at an equivalence ratio of 1. The Reynolds number is ~2.8×10^4. To explore the performance of the reduced mechanisms under gas turbine conditions, an inlet temperature of 600°C and pressure of 17atm was specified.

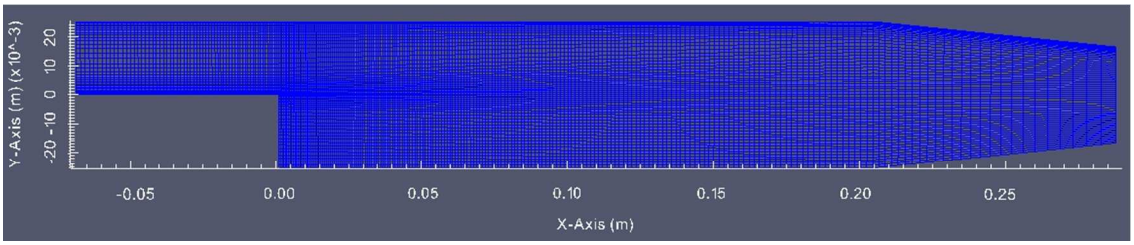
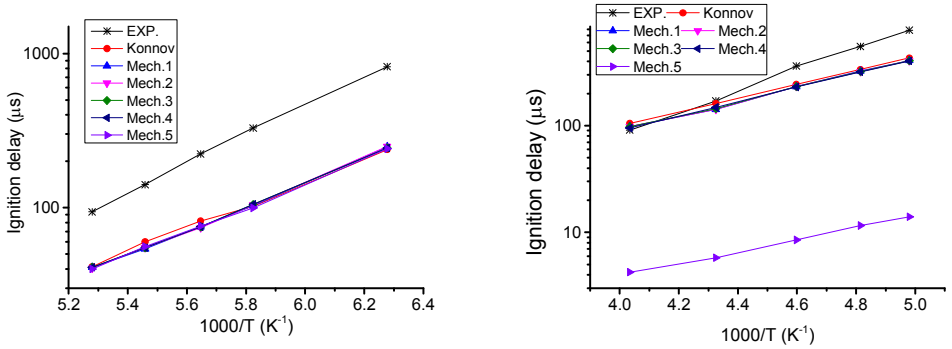


Figure 3. The geometry of the burner for turbulent combustion



a b

Figure 4. Ignition delay times of NH_3 mixtures (0.4%NH_3/0.6%O_2/99%Ar). a) 30.0 atm; b) 1.4 atm. Experiments from [31]

4 RESULTS AND DISCUSSION

4.1. Ignition Delay Times under High Pressure Conditions. Ignition delay times validation studies were conducted using Konnov's mechanism and the five different reduced mechanisms for several ammonia mixtures under different pressures. Figure 4 presents validation study results using ammonia-oxygen-argon mixtures. In Figure 4a, it can be seen that the prediction by the full Konnov mechanism and the reduced mechanisms present a considerable deviation from the experimental data, with average relative error around 63%. However, except for Mech. 5, accuracy is much better (average relative error around 27%.) at lower pressure, Figure 4b. Since the Konnov mechanism was developed under low pressure conditions, the results emphasize the necessity to optimize the detailed mechanism for ammonia combustion under higher pressure conditions. Nevertheless, it is noted that there is good correlation between the full and the reduced mechanisms. The validations for NH_3 is not so satisfying under high pressure conditions, this indicates improvements for ignition chemistry of pure NH_3 fuel are still needed.

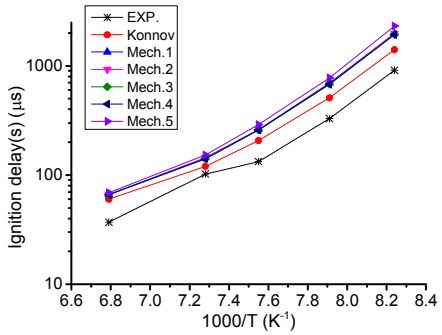
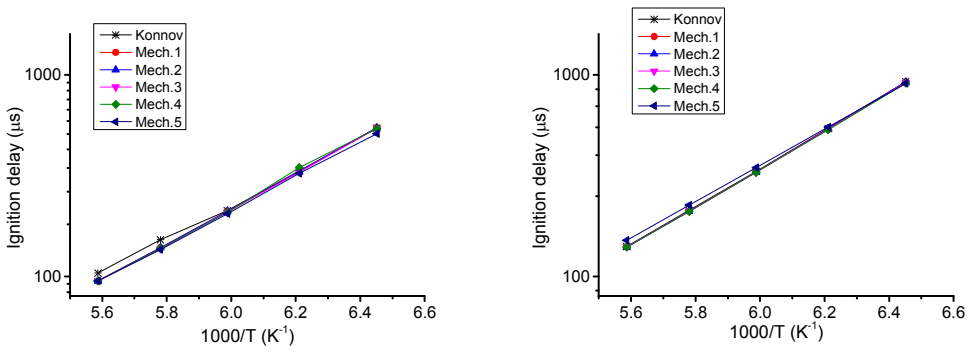
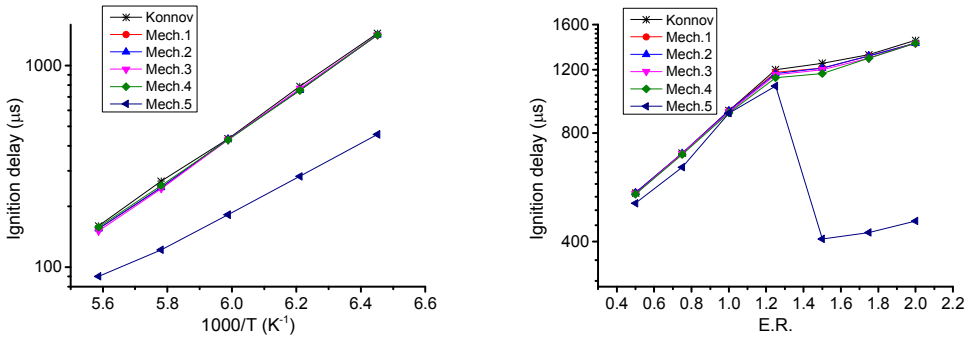


Figure 5. Ignition delay times of NH_3/CH_4 contained mixtures (0.02%NH_3/0.089%CH_4/0.297%H_2/0.297%CO/ 0.21%H_2O/0.157%CO_2/0.950%O_2/97.98%Ar) 12.0 atm, Experiments from [36].

Figure 5 shows the comparison between ignition-delay times of a NH_3 and CH_4 contained syngas mixture against predictions from Konnov's mechanism and the reduced mechanisms. Under the high pressure condition, the full and reduced mechanisms predict relatively longer ignition delay times compared to experimental data. Although Konnov's mechanism presents the shortest ignition delay time predictions, thus showing better prediction to the experimental data, the reduced mechanisms are close to Konnov's mechanism with relative deviation around 26.6%. These results suggest that the full and reduced mechanisms can have better performance in predicting ignition delay times of ammonia/methane combustion under gas turbine conditions than pure ammonia. The possible cause for the discrepancies can be either that the isothermal boundary conditions are not exactly the same or the idealization of homogeneity in the numerical calculation.





c d

Figure 6. Ignition delay times prediction of NH_3/CH_4 mixtures under gas turbine conditions (17atm) a) E.R.=0.5; b) E.R.=1; c) E.R.=2; d) E.R.=0.5-2, T=1550K.

To further assess the consistency of the reduced mechanisms with full Konnov's mechanism, ignition delay time predictions of ammonia/methane mixtures were performed under the pressure of 17atm to re-produce a typical ambient pressure inside a land-based gas turbine engine, as shown in Figure 6. In the simulation, ammonia/methane mixtures were diluted in 99%Ar under different equivalence ratios at a pressure of 17 atm. The mole fraction of ammonia and methane was set at 61% and 39%, respectively. This is the same ratio as that utilized in a generic swirl burner experimental campaign in [14]. As observed in Figure 6, in most cases, reduced mechanisms show good agreement to the full Konnov mechanism. However, Mech. 5 largely under-predicts the ignition delay times at an equivalence ratio of 2.0, Figure 6c. It is also observed that the equivalence ratio has a significant effect on the ignition delay time for ammonia/methane combustion blends. Figure 6d shows how ignition delay times increase with equivalence ratio. Except for Mech.5, all the other reduced mechanisms show good agreement with full Konnov's mechanism within the studied range of equivalence ratios between 0.5-2. The equivalence ratio effect on ignition delay times for NH_3/CH_4 mixture is obvious under high pressure conditions. The ignition delay times decrease with the increase of equivalence ratio condition. For instance, the factor between ignition delay times obtained at E.R. of 1 and E.R. of 0.5 is about 1.7 at 1670K whilst a larger factor of 1.9 was found between E.R. of 2 and E.R. of 1. There is very little previous research concerning ignition delay times of NH_3/CH_4 mixtures under high pressure conditions and experimental measurements in particular are required.

4.2. Validation of Major Species Predictions in Laminar Flames. To validate the performance of the full Konnov's mechanism and the reduced mechanisms for NH_3/CH_4 combustion, major products concentrations were predicted against experimental data from burner-stabilized premixed flames investigated by Tian[37], Figs 7-12. In these figures, R refers to the mole ratio of NH_3/CH_4. All the experimental and modelling work by Tian[37] studied premixed $NH_3/CH_4/O_2/Ar$ flames at low pressure of 4.0 kPa under stoichiometric conditions, the same combustion conditions are simulated in this study.

As observed in Figure 7 and 8, the concentration of CO and CO_2 decreases with R increasing, as expected, the decreasing trend resulting primarily from the reduced methane component in the NH_3/CH_4 mixture. The predicted and experimental data for CO and CO_2 show satisfactory agreement in general, with the larger discrepancy between experimental CO concentration and predictions. The average relative errors for CO and CO_2 are about 21% and 4% respectively for all the mechanisms considered. The concentration of major hydrogeneous products shown in Figures 7 and 8, whilst reproducing the same experimental trends, shows relative errors for H_2 and H_2O of around 41% and 45% respectively, emphasizing that the hydrogen chemistry still requires optimization. It also can be seen that R has a similar effect on H_2 as that on CO, whilst the concentration of H_2O increases with increasing R. Figures 11 and 12 show that Konnov's mechanism and most of the reduced mechanisms performance well in predicting the concentration of the two nitrous products. For the prediction of NO, the best performance is achieved by Mech.1 with relative error of 2.8% while Mech.5 overpredicted the NO concentration about 22%. It is clear that the quantities of N_2 and NO increase while augmenting R, as expected. To utilize ammonia and methane in gas turbine combustor, the emission of CO and NO of course will be an essential environmental concern. Although the above results are obtained under low pressure conditions and clearly some species predictions still need to be improved, nevertheless, the results still provide important information in assessing qualitatively the performance of NH_3/CH_4 combustion. Now that the concentrations of major products corresponding different mole ratios (R) of NH_3/CH_4 have been simulated, Konnov's mechanism and the reduced mechanisms can provide some insight into the NH_3/CH_4 combustion kinetics analysis to assist in optimizing the fuel mixture ratio for the study on gas turbine utilization.

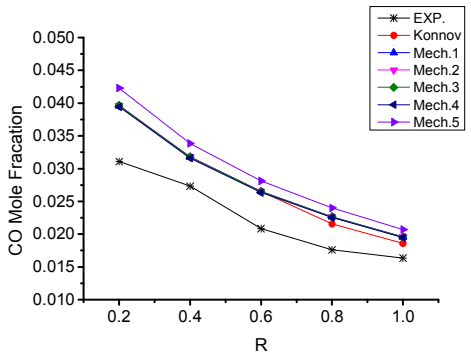


Figure 7. Final mole fraction of CO with different R

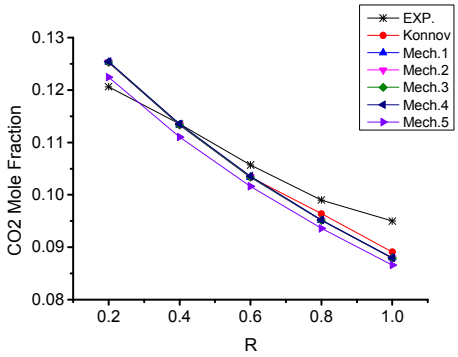


Figure 8. Final mole fraction of CO_2 with different R

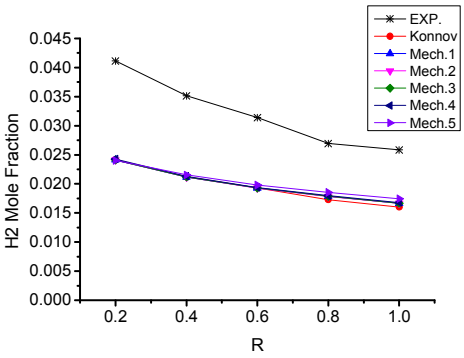


Figure 9. Final mole fraction of H_2 with different R

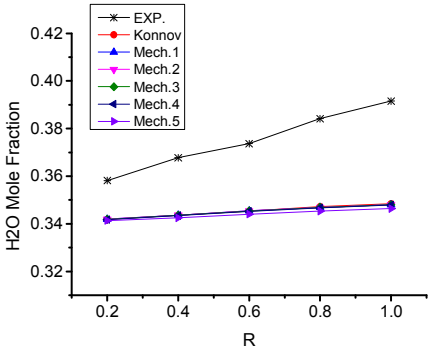


Figure 10. Final mole fraction of H_2O with different R

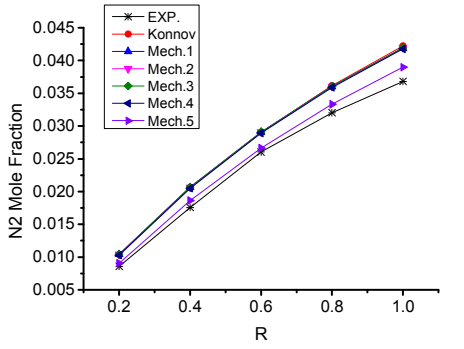


Figure 11. Final mole fraction of N_2 with different R

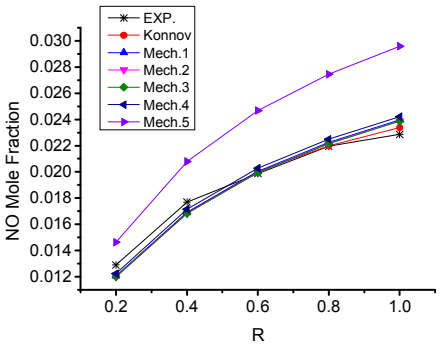


Figure 12. Final mole fraction of NO with different R

4.3. 2D Turbulent Combustion under Gas Turbine Conditions. To assess the applicability of the reduced mechanisms, CFD turbulent combustion simulations were performed with parallel computing technology, in which 64 cores were used during the calculation process with different reduced mechanisms. In terms of the processing time from ignition to steady state combustion, the shortest computational time was achieved with Mech. 5 taking 6.05h whilst Konnov's mechanism and Mech. 1-4 took 56.32h, 46.94h, 37.75h, 30.28h and 19.79h respectively. Figure 13 shows the temperature field for the turbulent flame simulation using full Konnov's mechanism. Along the dashed line ($y=-10^{-2}$ m), different parameters using the reduced mechanisms are compared in Figures 14-17.

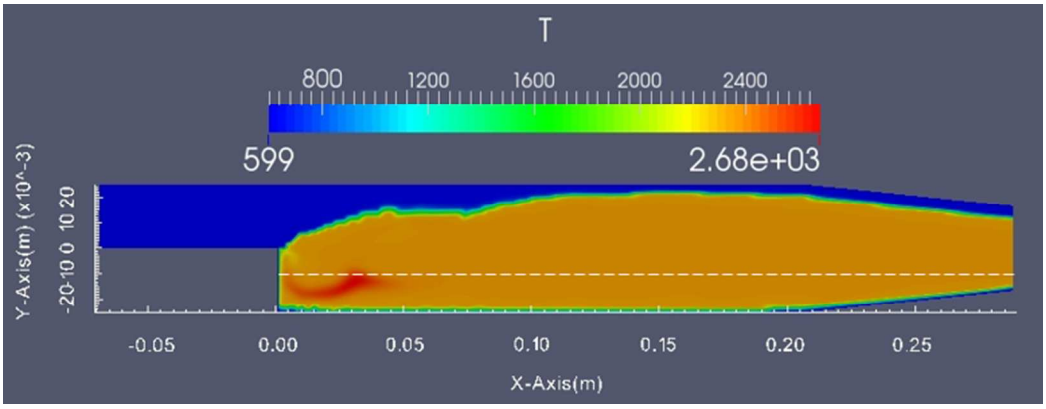


Figure 13. Temperature distribution calculation with Konnov mechanism

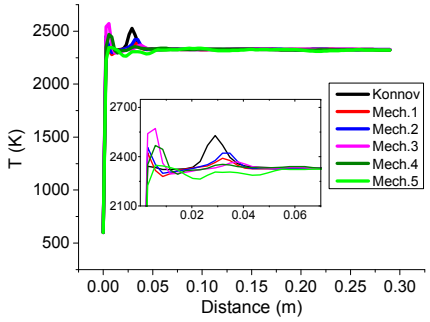


Figure 14. Computed profiles of temperature

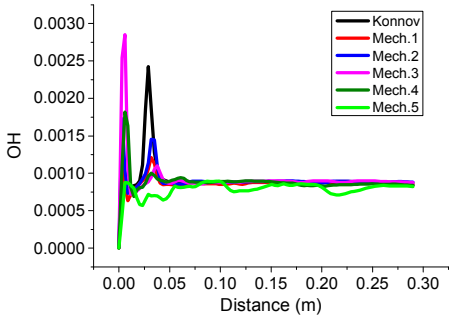


Figure 15. Computed profiles of OH mass fraction

Temperature profiles using the reduced mechanisms agree with Konnov's mechanism achieving ~2500K in the post flame zone, Figure 14. In Figure 15, most mechanisms predict good results for OH species concentration, but at small distances, Mech. 3 clearly predicts higher OH concentration than the Konnov mechanism, whilst Mech. 5 predicts a relatively lower OH concentration. Different magnitude and location of the OH peak indicate that flame fronts emerge at different locations, also accounting for differences in temperatures between simulations. Since the OH radical is a significant molecule through the combustion process of ammonia/methane fuels, these mechanisms can be used to carry out preliminary performance predictions towards combustion characterisation of such blends. However, it must be emphasized from the previous section that there is still work to do on new reaction mechanism to completely and accurately capture the reaction mechanism of ammonia/methane combustion.

Figure 16 and Figure 17 show emission prediction profiles using different mechanisms. As shown in Figure 16, in terms of exit CO emission concentration the five reduced mechanisms produce good agreement with the full Konnov's mechanism. At smaller distances, Mech. 3 shows higher peak value of CO emission than the Konnov mechanism, whilst other reduced mechanisms generate lower predictions. Moreover, Mech. 5 gives considerably higher predictions from distance 0.07 to 0.25. These trends suggest that the reduced mechanisms are adequate in predicting exhaust CO emission. To capture CO formation within the flame structure, the reduced mechanisms can cause some deviation from the full Konnov mechanism, especially Mech. 5. For NO emission, Mech.1-4 have predicted almost identical concentration profiles as the Konnov mechanism. Since NO is highly temperature sensitive, the reduced mechanisms show good potential for simulation using the complex chemistry coupled with turbulence.

Since NO emission is a major concern when utilizing ammonia combustion, pathway analyses and sensitivity analyses of NO formation were also conducted using Konnov's mechanism for this specific blend. As shown in Figure 18 and Figure 19, the most enhancing radical for NO formation is HNO, followed by NH and NH_2 radicals. Therefore, the profiles of the HNO radical were extracted using all the reduced mechanisms utilized. As expected, Mech.1-4 provide results comparable to Konnov's mechanism, while Mech.5 shows by far the largest discrepancy of more than 90%. The different fates of these amine species, as predicted by the reduced mechanisms, give rise to the different NO emission results, Figure 20.

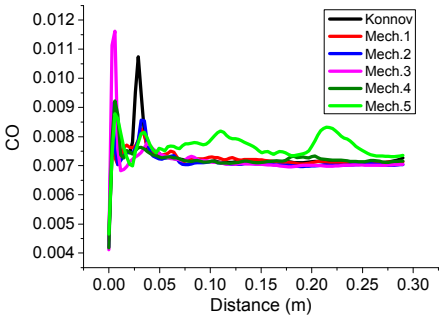


Figure 16. Computed profiles of CO mass fraction

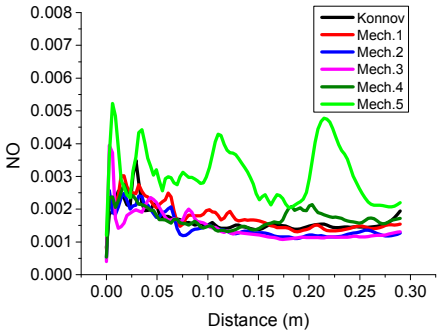


Figure 17. Computed profiles of NO mass fraction

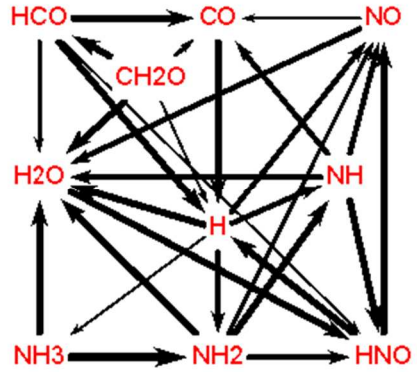


Figure 18. Reaction path of NO formation

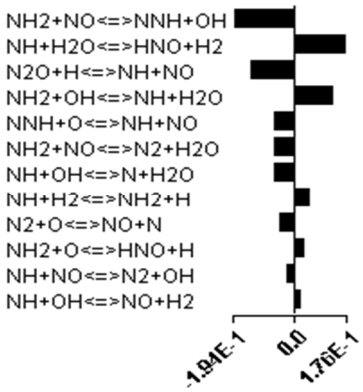


Figure 19. Normalized sensitivity of NO using Konnov's mechanism

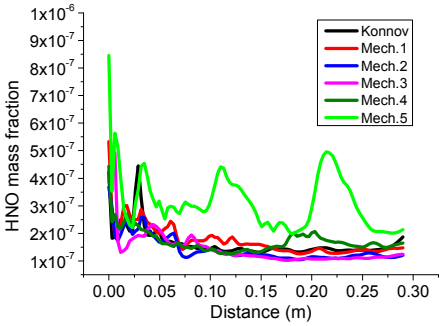


Figure 20. Computed profiles of HNO mass fraction

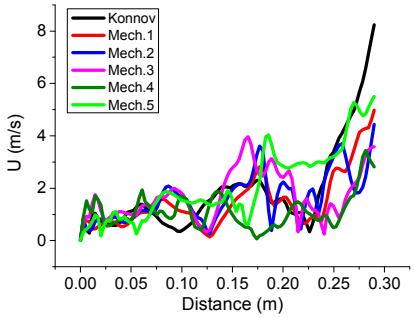


Figure 21. Computed profiles of velocity magnitude

Figure 21 shows velocity magnitude profiles along the dashed line. As chemical reactions interact with turbulence in the flame, the flow field will also be an essential indication for the performance of the mechanisms and the overall simulation. It can be seen that the predicted velocity magnitude fluctuates along the burner. Generally, all reduced mechanisms have given acceptable predictions compared to Konnov's mechanism. In this simulation of turbulent combustion, where turbulence and recirculation are take into account in the combustion process, all reduced mechanisms but Mech.5 show good performance under gas turbine conditions.

In general, most of the reduced mechanisms except Mech. 5 computed acceptable results compared with full Konnov's mechanism. This indicates that the reduced mechanisms Mech. 1-4 are qualified for the study of temperature field, exhaust emissions, flow field of the NH_3/CH_4 flame with 2D CFD modelling. From this study, overall Mech. 4 is recommended for future use in 3D CFD simulation, due to its relatively short computational time and reasonable accuracy.

5 CONCLUSION

In this study, five reduced chemical kinetic mechanisms based on Konnov's mechanism have been appraised with the aim of optimizing NH_3/CH_4 combustion in practical systems. The reduced mechanisms were examined using 0D, 1D and 2D models, under high temperature and pressure conditions, indicative of gas turbine combustors.

Ignition delay time calculations with reduced mechanisms for highly diluted ammonia under high pressure showed relatively larger deviations from the shock tube experimental data published previously, compared to low pressure conditions. Ignition delay time predictions for ammonia/methane contained blends showed that the reduced mechanisms provide reasonable agreement with experiment data. Furthermore, under high pressure (17atm) and different equivalence ratio conditions, ignition delay times predictions for ammonia/methane using Mech.1-4 demonstrated good performance against the full Konnov mechanism, while Mech.5 worked well for equivalence ratios in the range of 0.5 to 1.25 only. Also, combustion product calculations for NH_3/CH_4 in a burner-stabilized premixed flame showed good accuracy for all reduced mechanisms and the full Konnov's mechanism, which validates the capability of species concentration prediction. Finally, to assess the performance for use in practical CFD analyses, temperature profiles, OH radicals, CO, NO emissions and velocity magnitudes in a turbulent flame were predicted with reduced mechanisms under gas turbine conditions, all showing good agreement with those obtained through the full Konnov's mechanism apart from Mech.5.

In an overall assessment of the predictive capability of the reduced mechanisms for future CFD analysis, the model proposed for future ammonia/methane research is Mech.4, providing a good compromise between predictive capability compared to the full Konnov model and computational run-time..

SUPPORTING INFORMATION

The five reduced mechanisms in CHEMKIN format. This material is available free of charge via the Internet at http://pubs.acs.org.

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ACKNOWLEDGMENT

The authors would like to thank the support provided by the IT department and the Advanced Research Computing facility at Cardiff University (ARCCA). Moreover, Mr. Xiao would like to thank the China Scholarship Council for financial support of Ph.D. studies at the UK.

REFERENCES

(1) Zamfirescu, C.; Dincer, I., Using ammonia as a sustainable fuel. *Journal of Power Sources* **2008,** 185, (1), 459-465.

(2) Grannell, S. M.; Assanis, D. N.; Bohac, S. V.; Gillespie, D. E., The fuel mix limits and efficiency of a stoichiometric, ammonia, and gasoline dual fueled spark ignition engine. *Journal of Engineering for Gas Turbines and Power* **2008,** 130, (4), 042802.

(3) Zamfirescu, C.; Dincer, I., Ammonia as a green fuel and hydrogen source for vehicular applications. *Fuel Processing Technology* **2009,** 90, (5), 729-737.

(4) Frigo, S.; Gentili, R., Analysis of the behaviour of a 4-stroke Si engine fuelled with ammonia and hydrogen. *International Journal of Hydrogen Energy* **2013,** 38, (3), 1607-1615.

(5) Westlye, F. R.; Ivarsson, A.; Schramm, J., Experimental investigation of nitrogen based emissions from an ammonia fueled SI-engine. *Fuel* **2013,** 111, 239-247.

(6) Reiter, A. J.; Kong, S. C., Combustion and emissions characteristics of compression-ignition engine using dual ammonia-diesel fuel. *Fuel* **2011,** 90, (1), 87-97.

(7) Lear, W. E., *Ammonia-Fueled Combustion Turbines*, 2007 Annual NH3 Fuel Conference, 2007; NH3 Fuel Association: 2007.

(8) Karabeyoglu, A,; Evans, B., *Fuel Conditioning System for Ammonia Fired Power Plants*, 2012 Annual NH3 Fuel Conference, 2012; NH3 Fuel Association: 2012.

(9) Meyer, T.; Kumar; P., Li, M.; Redfern, K.; Diaz, D., *Ammonia Combustion with Near-Zero Pollutant Emissions*, 2011 Annual NH3 Fuel Conference, 2011; NH3 Fuel Association: 2011.

(10) Ganley, J; Bowery, M. S., *Engine-Ready, Carbon Free Ammonia Fuel.*, 2010 Annual NH3 Fuel Conference, 2010; NH3 Fuel Association: 2010.

(11) UNIDO, *Fertilizer Manual*. Kluwer Academic Publishers: The Netherlands, 1998.

(18) Platts, M., The Coke Oven By-Product Plant, http://www.accci.org/Byproduct.pdf.

(13) IFRF, Combustion Industry News, 2016, http://www.mnm.ifrf.net/mnm/article.html?aid=1529 [Accessed 25th May 2016]

(14) Valera-Medina, A.; Marsh, R.; Runyon, J.; Pugh, D.; Beasley, P.; Hughes, T.; Bowen, P., Ammonia–methane combustion in tangential swirl burners for gas turbine power generation. *Applied Energy* **2016**.

(15) Brackmann, C.; Alekseev, V. A.; Zhou, B.; Nordström, E.; Bengtsson, P.-E.; Li, Z.; Aldén, M.; Konnov, A. A., Structure of premixed ammonia + air flames at atmospheric pressure: Laser diagnostics and kinetic modeling. *Combustion and Flame* **2016,** 163, 370-381.

(16) Powell, O. A.; Papas, P.; Dreyer, C. B., Flame structure measurements of NO in premixed hydrogen–nitrous oxide flames. *Proceedings of the Combustion Institute* **2011,** 33, (1), 1053-1062.
(17) Kumar, P.; Meyer, T. R., Experimental and modeling study of chemical-kinetics mechanisms for H2–NH3–air mixtures in laminar premixed jet flames. *Fuel* **2013,** 108, 166-176.
(18) Shmakov, A. G.; Korobeinichev, O. P.; Rybitskaya, I. V.; Chernov, A. A.; Knyazkov, D. A.; Bolshova, T. A.; Konnov, A. A., Formation and consumption of NO in H2+O2+N2 flames doped with NO or NH3 at atmospheric pressure. *Combustion and Flame* **2010,** 157, (3), 556-565.
(19) Konnov, A. A., Implementation of the NCN pathway of prompt-NO formation in the detailed reaction mechanism. *Combustion and Flame* **2009,** 156, (11), 2093-2105.
(20) Duynslaegher, C.; Contino, F.; Vandooren, J.; Jeanmart, H., Modeling of ammonia combustion at low pressure. *Combustion and Flame* **2012,** 159, (9), 2799-2805.
(21) Nozari, H.; Karabeyoğlu, A., Numerical study of combustion characteristics of ammonia as a renewable fuel and establishment of reduced reaction mechanisms. *Fuel* **2015,** 159, 223-233.
(22) Duynslaegher, C.; Jeanmart, H.; Vandooren, J., Ammonia combustion at elevated pressure and temperature conditions. *Fuel* **2010,** 89, (11), 3540-3545.
(23) Duynslaegher, C.; H. J., Kinetics in ammonia-containing premixed flames and a preliminary investigation of their use as fuel in spark ignition engines. *Combustion science and techanology* **2009,** 181, 1092-1106.
(24) Sun, W.; Chen, Z.; Gou, X.; Ju, Y., A path flux analysis method for the reduction of detailed chemical kinetic mechanisms. *Combustion and Flame* **2010,** 157, (7), 1298-1307.
(25) Gou, X.; Sun, W.; Chen, Z.; Ju, Y., A dynamic multi-timescale method for combustion modeling with detailed and reduced chemical kinetic mechanisms. *Combustion and Flame* **2010,** 157, (6), 1111-1121.
(26) Advanced Combustion and Propulsion Lab http://engine.princeton.edu/ (accessed Apr 4, 2016).
(27) Schultz E, S. J. *Validation of detailed reaction mechanisms for detonation simulation*; California Institute of Technology: Pasadena, CA, 2000.
(28) Chaos, M.; Dryer, F. L., Syngas combustion kinetics and applications. *Combustion Science and Technology* **2008,** 180, (6), 1053-1096.
(29) Herzler, J.; Naumann, C., Shock-tube study of the ignition of methane/ethane/hydrogen mixtures with hydrogen contents from 0% to 100% at different pressures. *Proceedings of the Combustion Institute* **2009,** 32, (1), 213-220.
(30) Reaction Workbench 15131, Reaction Design: San Diego, 2013.
(31) Mathieu, O.; Petersen, E. L., Experimental and modeling study on the high-temperature oxidation of Ammonia and related NOx chemistry. *Combustion and Flame* **2015,** 162, (3), 554-570.
(32) Strohle, J.; Myhrvold, T., An evaluation of detailed reaction mechanisms for hydrogen combustion under gas turbine conditions. *International Journal of Hydrogen Energy* **2007,** 32, (1), 125-135.
(33) Olm, C.; Zsély, I. G.; Pálvölgyi, R.; Varga, T.; Nagy, T.; Curran, H. J.; Turányi, T., Comparison of the performance of several recent hydrogen combustion mechanisms. *Combustion and Flame* **2014,** 161, (9), 2219-2234.
(34) Pfahl, U. J.; Ross, M. C.; Shepherd, J.E.; Pasamehmetoglu, K. O.; Unal, C., Flammability Limits, Ignition Energy and Flame Speeds in H2-CH4-NH3-N2O-O2-N2 Mixtures. *Combustion and Flame* **2000,** 123, (1–2), 140–158.
(35) Huang, J.; Hill, P. G.; Bushe, W. K.; Munshi, S. R., Shock-tube study of methane ignition under engine-relevant conditions: experiments and modeling. *Combustion and Flame* **2004,** 136, (1-2), 25-42.
(36) Mathieu, O.; Kopp, M. M.; Petersen, E. L., Shock-tube study of the ignition of multi-component syngas mixtures with and without ammonia impurities. *Proceedings of the Combustion Institute* **2013,** 34, (2), 3211-3218.
(37) Tian, Z.; Li, Y.; Zhang, L.; Glarborg, P.; Qi, F., An experimental and kinetic modeling study of premixed NH3/CH4/O2/Ar flames at low pressure. *Combustion and Flame* **2009,** 156, (7), 1413-1426.
(38) Goodwin, D. G.; Moffat, H.K.; Speth, R. L., Cantera: An object- oriented software toolkit for chemical kinetics, thermodynamics, and transport processes. http://www.cantera.org, 2016. Version 2.2.1. In.
(39) Weller, H, G,; Tabor, G.; Jasak, H,; Fureby, C., A tensorial approach to computational continuum mechanics using object-oriented techniques. *Computers in Physics,* **1998,** 12 (1997), 620–631.
(40) Duwig, C.; Nogenmyr, K. J.; Chan, C. K.; Dunn, M. J., Large Eddy Simulations of a piloted lean premix jet flame using finite-rate chemistry. *Combustion Theory and Modelling* **2011,** 15, (4), 537-568.